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Desalination 204 (2007) 24–32

DESALINATION

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Hydrocarbon removal from industrial wastewater by hollow-fibre membrane bioreactors

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Received 4 May 2006; accepted 10 May 2006

Abstract

Membrane bioreactors have been extensively studied for the treatment of domestic wastewater. In this paper we describe the application of membrane bioreactors for the depuration of non-civil wastewater coming from the washing of mineral oil storage tanks. Microfiltration hollow-fibre membranes were submerged in the bioreactor where the biomass used the hydrocarbon as a substrate. The performance of the submerged membrane bioreactor was analysed in terms of COD and hydrocarbon removal during different experiments that showed the high efficiency of the system. Particular care was taken in carrying out the operations in the sub-critical flux region. The reactor performance was very high, with removal efficiencies ranging between 93% and 97%, also when the concentration of hydrocarbon was very high. Moreover, the hydraulic retention times used in this work were lower compared to those used in an activated sludge process. Some kinetic parameters for the COD and the hydrocarbon removal were assessed.

Keywords: Membrane bioreactors; Submerged hollow-fibre membranes; Microfiltration; Hydrocarbon removal

1. Introduction

Membrane bioreactors (MBR) have been studied since the '60s and during the last ten years

the number of scientific papers on the topic has been steadily increasing [1]. The main application of MBR is the treatment of civil wastewater [2–5]. Recently the reserachers' attention has shifted to the application of MBR to industrial waste-

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Presented at EuroMed 2006 conference on Desalination Strategies in South Mediterranean Countries: Cooperation between Mediterranean Countries of Europe and the Southern Rim of the Mediterranean. Sponsored by the European Desalination Society and the University of Montpellier II, Montpellier, France, 21–25 May 2006.

water. Of particular interest is the treatment of industrial wastewater containing mineral oil [6,7], hospital and pharmaceutical [8–10], agrofood [11, 12] and textile [13] wastewater.

The role of the membrane is to avoid the passage of the biomass in the effluent, for this purpose microfiltration membranes are selective enough to retain the suspended solids, which constitute the biomass. Both tubular and hollow-fibre membranes are currently used for MBR. Tubular membranes are usually assembled in an external unit. One advantage of the hollow-fibre membranes is that they can be easily and directly submerged in the bioreactor volume. When submerged hollow-fibre membranes are used, the clarified effluent is obtained by means of a dead-end filtration by applying transmembrane pressure. It is clear that one of the limiting factors in the MBR can be the biomass adhesion to the membrane surface, and that in order to maintain the operations stable and long-term before the membrane cleaning the permeate flux should be maintained below the critical flux [14].

The advantages of using MBR against conventional activated sludge processes are the strong reduction of the plant volume, the possibility of using higher biomass concentrations (between 5 and 17 g/L), the reduction of the waste sludge amount and the possibility of continuous operations [2].

In this work we are going to show preliminary results of a submerged hollow-fibre membrane bioreactor for the treatment of wastewater containing mineral hydrocarbons. The aim of the work is to assess the bioreactor performance and characteristics when the permeate flux is not affected by biofouling.

2. Experimental

2.1. Wastewater characteristics and conventional treatments

Industrial wastewater containing hydrocarbons was provided by a local company that supplies

services for the storage of mineral oil as well as for its loading and unloading in the industrial port of Genoa. The water from the storage tank wash contains a high concentration of hydrocarbons and organic compounds. The organic compound composition of the washing water depends on the type of products stored in the tanks and both the frequency and quality of the washings. Some of the organic compounds are very soluble in water (e.g. cyclohexanone) while others are almost insoluble (e.g. xylenes). Before a biological treatment process, wastewater is treated in a skimming tank to remove the oil floating on its surface. In the conventional biological treatment wastewater is kept in contact with the activated-sludge for 2–3 days with a mixed liquor suspended solid (MLSS) concentration between 2 and 4 g/L. Finally, the effluent is treated in a physical-chemical unit. The washing water for our experiments was sampled after the skimming tank. This last wastewater had a pH in the range of 6.5–8.5. The hydrocarbon concentration was between 33 and 9000 mg/L and the chemical oxygen demand (COD) varied from 700 to 10,000 mg/L.

In Table 1 some of the characteristics of the used wastewater are resumed. Nitrogen as ammonia was also present in concentrations ranging from 114 to 330 mg/L. Phosphorus as phosphate and other forms of nitrogen (as nitrate or nitrite) were absent.

2.2. Experimental set-up and operating conditions

Fig. 1 shows the experimental set-up. The membrane bioreactor (MBR) was composed of a wastewater tank that fed the biological reactor that contained a submerged membrane module. An air diffuser was located under the membrane module to provide the oxygen and the required turbulence on the membrane surface, necessary to suspend the activated sludge in the reactor volume ($V = 3$ L). The reactor was equipped with a dissolved oxygen sensor (mod. 027IP15, B&C electronics), a thermocouple and a pH electrode (mod. A773792, Phonix Electrode Co.). If necessary,

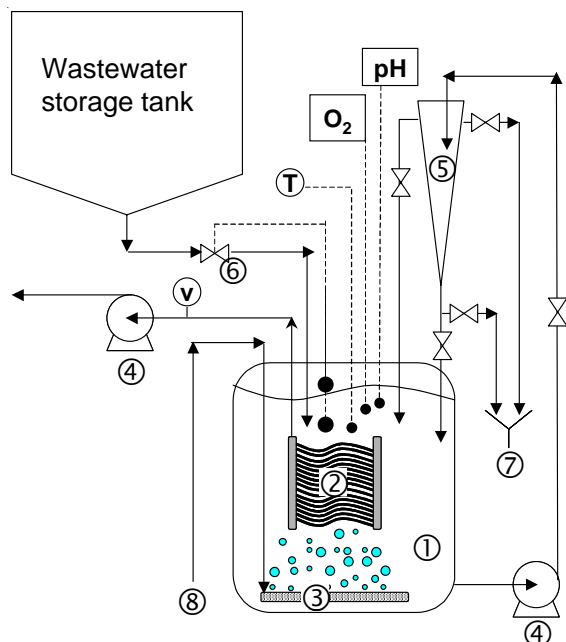


Fig. 1. Experimental set-up used as membrane bioreactor. (1) bioreactor tank; (2) membrane module; (3) air diffuser; (4) peristaltic pumps; (5) settling tank; (6) electrovalve driven by a level-meter; (7) sludge and clarified water drain; (v) vacuum; (O_2) oxygen sensor; (pH) ph-meter; (T) thermocouple.

part of the activated sludge could be wasted or recycled by a peristaltic pump into the settling tank located before the reactor. The treated wastewater effluent was recovered by filtration through the microfiltration membrane where the driving force was provided by a peristaltic pump located after the membrane module. The level in the reactor tank was kept constant using a level sensor coupled with an electrovalve on the feed stream. The activated-sludge was obtained by the inoculation of a sample of the same activated sludge from the conventional process. The biomass used was composed of non-pathogenic micro-organisms in aqueous solution with peptones and mineral salts. As mentioned before nitrogen was present in wastewater only as NH_3-N , and phosphorus was absent. Nitrogen and

phosphorus were added in the mixed liquor as NH_4NO_3 and KH_2PO_4 respectively, using the concentrations suggested by the micro-organism supplier.

The membranes used were symmetric micro-filtration hollow-fibre. The outer and the inner diameters were 0.65 and 0.41 mm respectively. The nominal pore size of the membrane was $0.4 \mu m$. Fig. 2 shows a cross-section (a) and the surface morphology of the membrane (b) obtained using a scanning electron microscope (Leo Stereoscan 440). The hollow-fibre membranes were arranged in a module in order to have a membrane area of $0.2 m^2$. Fig. 2c shows the module. The manifolds collecting the water filtered by the membranes were made of polypropylene and a sealing procedure with a proper resin had been developed in order to avoid any problems related to the membrane–drain joint.

During the experiments some parameters were determined in order to quantitatively monitor the reactor performance. Total hydrocarbons concentration (THC) by CCl_4 extraction, chemical oxygen demand (COD) using the dichromate method, mixed liquor suspended solids (MLSS)

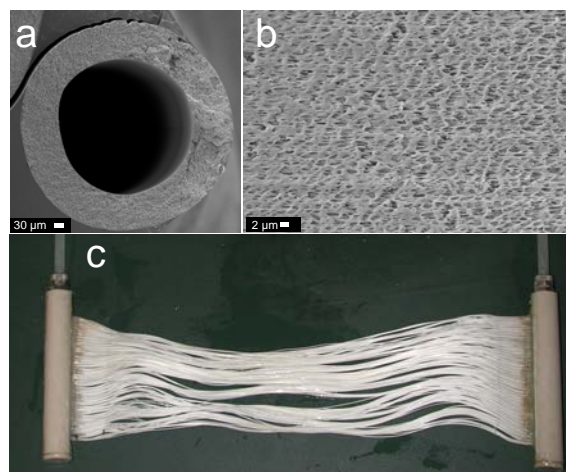


Fig. 2. Scanning electron microscopy images of (a) a cross-section and of (b) the hollow-fibre membrane outer surface; (c) hollow-fibre membrane module.

by filtration on a 0.2 μm filter and weight measurements and ammonia using the Nessler method were determined in the feed and in the membrane permeate, following the analytical procedures reported in the APHA standard methods [15]. The concentration of the nutrients as nitrate, nitrite and phosphate ions had been checked in the mixed liquor using an ion exchange chromatograph (DX 120 Dionex equipped with an Ion-pac AS9-HC column).

Table 1 resumes the main operating conditions of the membrane bioreactor during the runs studied. Between the two consecutive runs the membrane module was cleaned in a solution of NaOCl (500 mg/L as chlorine) at 40°C for 2 h.

3. Results and discussion

3.1. Membrane and biofouling

The accumulation of biomass on the membrane surface can strongly affect the membrane performance [16]. Depending on the biomass concentration, the permeate flux increases with the increasing transmembrane pressure. When the critical flux is reached the permeate flux does not increase proportionally with the pressure and above the critical flux the biomass accumulation on the membrane becomes a limiting factor [17, 18]. Some experiments based on the measure-

ment of the transmembrane pressure were carried out in order to estimate the critical flux in our operating conditions. As shown in Fig. 3, the critical flux for the membrane module used with the typical biomass concentrations was between 3 and 5 $\text{L m}^{-2} \text{h}^{-1}$. All the runs were then carried out in the sub-critical flux region with permeate flux ranging from 0.4 to 1.5 $\text{L m}^{-2} \text{h}^{-1}$.

The membrane module was cleaned between two consecutive runs and the water flux was measured and compared with that of the new membrane. The results obtained are reported in Fig. 3 in terms of water flux through the membrane as a function of the applied transmembrane pressure (TMP) applied. In the new membrane the water flux increased linearly with the TMP until about 8 kPa. The water flux in the membrane, after being used and without any washing procedures, was almost the same of the new membrane until 5 kPa, and after the water flux reached a plateau. This indicated that the biomass fouled the membrane surface. In the high transmembrane pressure region the water flux could be partially recovered by a cleaning procedure based on a dilute solution of NaOCl. Moreover the water flux curve after a cleaning procedure was not dependent on the run conditions in which the membrane operated in the bioreactor. It is likely that even in the sub-critical flux region (where the permeate flux was not affected) the suspended solids accumulated on the

Table 1
Pilot testing conditions

Operating condition	1st run	2nd run	3rd run	4th run
Single run operating time (progressive operating time), h	160 (0–160)	270 (200–470)	360 (500–860)	1200 (900–2100)
Temperature, °C	22	22	22	22
pH	6–8	6–8	6–8	6–8
Permeate flux, $\text{L}/(\text{m}^2 \text{h})$	0.83	0.42	1.25	1.5
Hydraulic retention time, h	17.7	31.8	11.5	9.7
Average mixed liquor suspended solids (MLSS range), g/L	5.2 (4.8–7.4)	8.4 (7.4–9)	9.2 (7.3–11)	14 (8–17)
Average COD, mg/L	1300	7964	1800	1400
Average total hydrocarbons, mg/L	1436	7500	1350	900

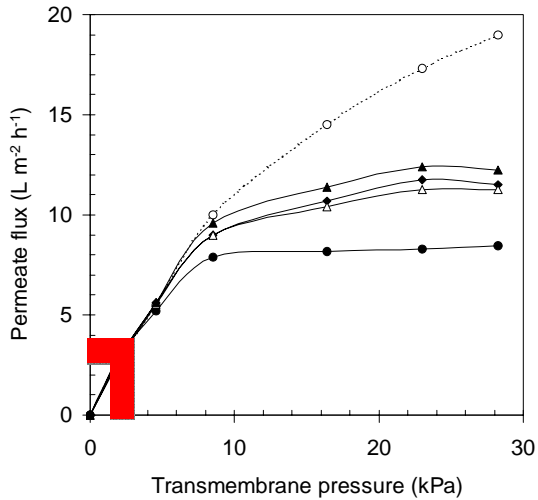


Fig. 3. Water flux of the membrane module before the beginning of the experiments (○), after a typical run without any cleaning procedures (●), after different runs and after cleaning with a dilute solution of NaOCl at 40°C for 2 h (◆, ▲, △).

membrane surface as well as in some pores.

3.2. Membrane bioreactor performance

Figs. 4 and 5 show the substrate concentration in the feed and in the permeate in terms of COD (Fig. 4) or total hydrocarbon concentration (Fig. 5)

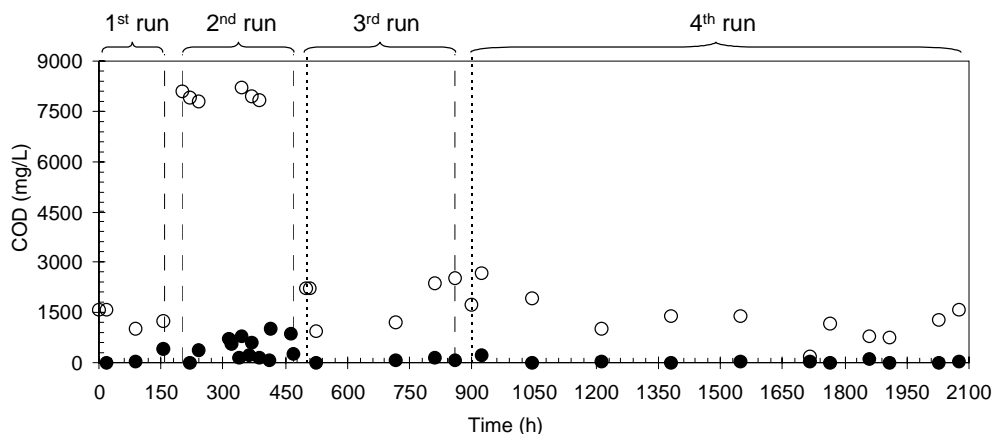


Fig. 4. COD in the feed (○) and in the permeate (●) for 4 consecutive runs.

as a function of the operating time. The substrate concentration in each run was not always the same and moreover a little scatter was present in the concentration data, due to the sometimes high dilution ratio used for the analytical measurements. These results are resumed in Table 2 in terms of average substrate concentration for each run period. Almost all the COD was due to the hydrocarbon present in the wastewater. The removal efficiency of both COD and hydrocarbons was between 93% and 96% also when the substrate concentration was very high (e.g. 2nd run). The highest and the lowest volumetric organic loadings applied were about $6 \text{ kg}_{\text{COD}} \text{ m}^{-3} \text{ h}^{-1}$ and $1.7 \text{ kg}_{\text{COD}} \text{ m}^{-3} \text{ h}^{-1}$ respectively.

Fig. 6 shows the results of two batch experiments where the mixed liquor suspended solids (which represent an index of the biomass in the reactor) are reported against the time. The biomass increased with time and then reached the stationary phase. By examining the first part of the curve an exponential growth law could be inferred

$$X = X_0 e^{\mu^{\max} t} \quad (1)$$

where X is the biomass concentration and μ^{\max} is the maximum specific growth rate t is the time. The average μ^{\max} , calculated from different batch

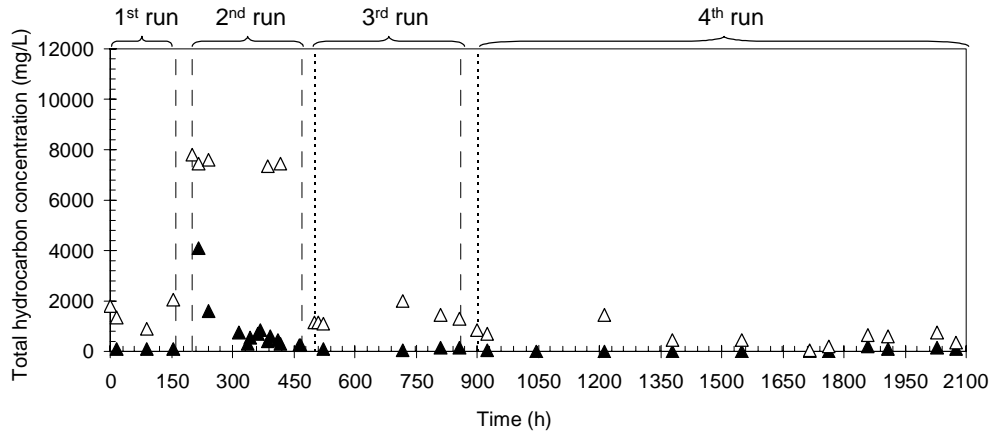


Fig. 5. Total hydrocarbon concentration in the feed (Δ) and in the permeate (\blacktriangle) for 4 consecutive runs.

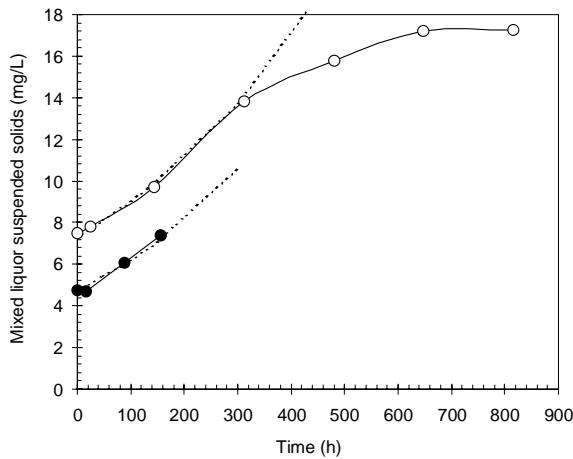


Fig. 6. Mixed liquor suspended solids for two batch runs with different starting biomass concentrations and corresponding biomass exponential growth curves (broken lines).

experiments with different starting biomass concentrations, was $0.024 \pm 0.03 \text{ h}^{-1}$. Fig. 6 shows the curve of X fitting the experimental data of the first part of the growth curve.

The results of the continuous runs could be analysed considering that the specific utilization rate U could be calculated as follows:

$$U = \frac{S_i - S_p}{X \cdot \text{HRT}} \quad (2)$$

where S_i and S_p are the inlet and the outlet substrate concentrations respectively, X is the biomass concentration and HRT is the hydraulic retention time.

Obviously U would depend on the substrate concentration and assuming the Monod equation for the biomass growth to be:

$$\mu = \mu^{\max} \frac{S}{K_s + S} \quad (3)$$

with μ the specific growth rate and K_s the half-velocity constant, we have

$$U = \frac{\mu^{\max}}{Y} \frac{S}{K_s + S} = k \frac{S}{K_s + S} \quad (4)$$

where Y is the maximum yield coefficient.

By a linearization of the above equation, K_s could be calculated. By considering COD as substrate k was about $45 \text{ mg}/(\text{g}\cdot\text{h})$ and K_s was about 170 mg/L . For hydrocarbons as substrate k was $44 \text{ mg}/(\text{g}\cdot\text{h})$ and K_s was 215 mg/L respectively. In Fig. 7 the experimental specific utili-

Table 2
Average substrate concentration in the feed and permeate of each run

Run	Time (h)	Hydraulic retention time (h)	Total wastewater volume (L)	Mixed liquor suspended solids (g/L)	COD			Total hydrocarbon		
					Feed (mg/L)	Permeate (mg/L)	Removal efficiency (%)	Feed (mg/L)	Permeate (mg/L)	Removal efficiency (%)
1st	160	17.7	27.1	5.2	1300	80	93.8	1436	101	93.0
2nd	270	31.8	25.4	8.4	7964	268	96.6	7500	350	95.3
3rd	360	11.5	94.0	9.2	1800	90	95.0	1350	95	93.0
4th	1200	9.7	370.6	14	1400	48	96.4	900	35	96.1

zation rate for the four runs is plotted against both the outlet substrate concentration (a) and the outlet substrate/biomass ratio (b). It could be observed that for high outlet substrate/biomass ratio the specific utilization rate declined since the substrate became a limiting factor and the bioreaction rate tended to be of first-order.

Finally we observed that when the bioreactor operated in the proximity or in the stationary phase

of the curve the amount of excess sludge was considerably reduced. In this condition the substrate removal efficiency was very high confirming that one of the advantages of using MBR rather than conventional activated sludge lies in the possibility of operating with high biomass concentrations with lower reactor volumes, high removal efficiency and low waste sludge amount.

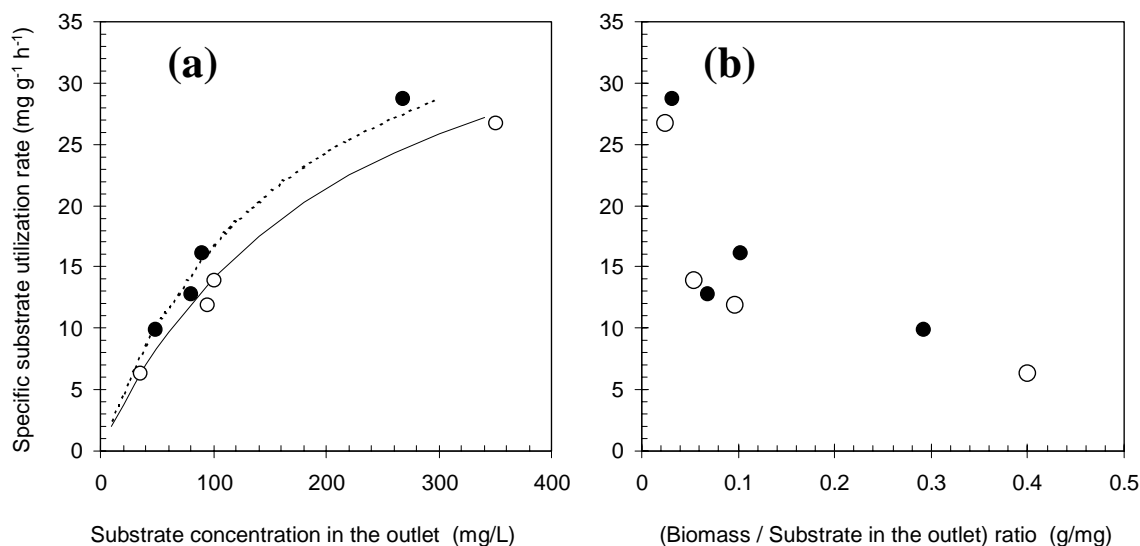


Fig. 7. Specific substrate utilization rate as a function of both (a) the outlet substrate concentration, and (b) the (biomass/outlet substrate concentration ratio). (●) The substrate is the COD (mg/L); (○) the substrate is the total hydrocarbon concentration. The broken and the continuous curves are calculated on the fitted parameters (k and K_s).

4. Conclusions

The treatment of wastewater containing hydrocarbons was carried out using a membrane bioreactor. The role of the membrane was to clarify by dead-end filtration the mixed liquor. The membrane module realized using hollow-fibre membranes was submerged directly in the bioreactor. Then the performance of the bioreactor was studied with permeating fluxes below the critical flux (beyond the critical flux the accumulation of the biomass on the membrane could not be neglected). In the sub-critical flux region a little amount of biomass remained adherent to the membrane even after the cleaning procedures. In any case this residual biomass did not strongly affect the membrane performance in the bioreactor during the runs.

The reactor performance was very high, with removal efficiencies ranging between 93% and 97% also when the concentration of hydrocarbon was very high. Moreover, the hydraulic retention times (2–3 days) used in this work were lower compared to those used in the activated sludge process. Some kinetic parameters for the COD and the hydrocarbon removal were assessed. These parameters will be useful for the ongoing research aimed at better understanding the limits and further potentialities of the membrane bioreactor for the application studied.

Acknowledgements

We acknowledge Attilio Carmagnani S.p.A., Genoa, Italy, that supplied us the wastewater and the activated sludge used in this work.

References

- [1] W. Yang, N. Cicek and J. Ilg, State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America, *J. Membr. Sci.*, 270 (2006) 201–211.
- [2] M. Gander, B. Jefferson and S. Judd, Aerobic MBRs for domestic wastewater treatment: a review with cost considerations, *Separ. Purif. Technol.*, 18 (2000) 119–130.
- [3] S. Zhang, R. Van Houten, D.H. Eikelboom, H. Doddema, Z. Jiang, Y. Fan and J. Wang, Sewage treatment by a low energy membrane bioreactor, *Biores. Technol.*, 90 (2003) 185–192.
- [4] T.I. Yoon, H.S. Lee and C.G. Kim, Comparison of pilot scale performances between membrane bioreactor and hybrid conventional waste water treatment system, *J. Membr. Sci.*, 242 (2004) 5–12.
- [5] S.H. Yoon, H.S. Kim and I.T. Yeom, The optimum operational condition of membrane bioreactor (MBR): cost estimation of aeration and sludge treatment, *Water Res.*, 38 (2004) 37–46.
- [6] W. Scholz and W. Fuchs, Treatment of oil contaminated waste water in a membrane bioreactor, *Water Res.*, 14 (2000) 3621–3629.
- [7] C. Cheng, D. Phipps and R.M. Alkhattar, Treatment of spent metalworking fluids, *Water Res.*, 17 (2005) 4051–4063.
- [8] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger and H. Kroiss, Removal of selected pharmaceutical, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants, *Water Res.*, 39 (2005) 4797–4807.
- [9] X. Wen, H. Ding, X. Huang and R. Liu, Treatment of hospital waste water using a submerged membrane bioreactor, *Process Biochem.*, 39 (2004) 1427–1431.
- [10] M. Petrovic, S. Gonzalez and D. Barceló, Analysis and removal of emerging contaminants in wastewater and drinking water, *Trends Anal. Chem.*, 10 (2003) 685–696.
- [11] Y. Wang, X. Huang and Q. Yuan, Nitrogen and carbon removals from food processing waste water by an anoxic/aerobic membrane bioreactor, *Process Biochem.*, 40 (2005) 1733–1739.
- [12] P. Artiga, E. Ficara, F. Malpei, J.M. Garrido and R. Mendez, Treatment of two industrial waste water in a submerged membrane bioreactor, *Desalination*, 179 (2005) 161–169.
- [13] B. Van der Bruggen, E. Curcio and E. Drioli, Process intensification in the textile industry: the role of membrane technology, *J. Environ. Manag.*, 73 (2004) 267–274.
- [14] A. Pollice, A. Brookes, B. Jefferson and S. Judd, Sub-critical flux fouling in membrane bioreactors: a review of recent literature, *Desalination*, 174 (2005) 221–230.
- [15] AWWA, WEF, APHA, Standard Methods for Ex-

- amination of Water and Wastewater, XVIII ed., Washington, DC, 1992.
- [16] I.S., Chang and S.N. Kim, Wastewater treatment using membrane filtration — effect of biosolids concentration on cake resistance, *Process Biochem.*, 40 (2005) 1307–1314.
- [17] S. Ognier, C. Wisniewski and A. Grasmick, Membrane bioreactor fouling in sub-critical filtration conditions: a local flux concept. *J. Membr. Sci.*, 229 (2004) 171–177.
- [18] J.A. Howell, H.C. Chua and T.C. Arnot, In situ manipulation of critical flux in a submerged membrane bioreactor using variable aeration rates, and effects of membrane history, *J. Membr. Sci.*, 242 (2004) 13–19.